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Putting the squeeze on energetic materials – structural characterisation of a high-pressure phase of CL-20**

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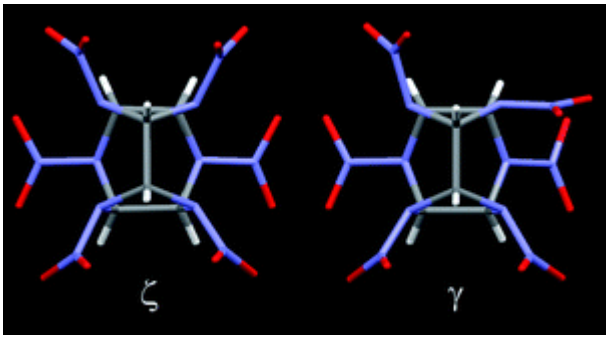
Supporting information:
[†] CCDC reference number 765864. For crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/C002701D

Graphical abstract:



Abstract

The crystal structure of the high-pressure ζ-form of the high explosive CL-20 has been determined using a combination of x-ray single crystal and powder diffraction techniques.

Main text

Energetic materials are defined as those that release heat and, generally, gaseous products upon stimulus by heat, impact, shock, spark, etc.[1] The performance of energetic materials can depend on a number of factors that include: sensitivity to detonation by stimulus; the detonation velocity; the chemical reactivity; the thermal stability; and crystal density. Polymorphism and solid-state phase transitions in these materials may therefore have significant consequences and the performance of an energetic formulation may be highly dependent on the particular polymorph that is used. In order to effectively model the behaviour of energetic materials under operational conditions it is essential to obtain detailed structural information for these compounds. In many cases, the crystal structure obtained under ambient conditions is used as the basis for modelling properties at higher temperatures and pressures because structural information is not available at more extreme conditions. However it is well-documented that such extreme conditions can often lead to substantial changes in intermolecular interactions and molecular geometries, and can even induce phase transitions. It is for this reason that we have initiated a programme of research to identify and structurally characterise polymorphs of energetic materials obtained at high pressures and/or temperatures and to examine the effect of pressure and temperature on the intermolecular interactions in these materials. We have recently determined the structures of three polymorphs of the widely used military explosive RDX (1,3,5-trinitrohexahydro-1,3,5-triazine): the high-pressure γ-form,[2] the highly metastable β-form obtained at ambient conditions,[3] and the polymorph obtained at high temperatures and pressures (ε-RDX).[4]

These studies have been extended to investigate the polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW) shown in Figure 1, and which is also known as CL-20 on account of its development at China Lake, USA.[5] CL-20 is the most powerful explosive in current use although some concerns remain over its sensitivity to detonation.[6] Its high performance and high density have been attributed to the 1:1 ratio of C atoms to nitramine groups and to its caged molecular structure.[7]

The behaviour of CL-20 at variable temperature and pressure has been extensively explored using optical microscopy and vibrational spectroscopy to characterise five forms,[8] although the α-form has subsequently been shown to be a hydrate.[5] All of these forms are stable at ambient temperature and pressure and have been structurally characterised.[5] The most stable and densest form under ambient conditions is the ε-form[9] and the structural effects of compression on this form have been studied by both

experimental[10,11] and computational methods.[12,13] Compression of the γ-form above 0.7(5) GPa identified a ζ-form,[8] and an energy dispersive x-ray diffraction attempted to identify this form.[14] In a very thorough x-ray powder diffraction study of CL-20 by Gump *et al*., the authors successfully identified the ζ-form at pressures above 0.9 GPa, but attempts to determine its structure were unsuccessful.[10,11] Recent spectroscopic studies have suggested that compression of the ε-form gives the γ-form between 4.1 and 6.4 GPa and that subsequent compression of this sample leads to the ζ-form at much higher pressures (~18.7 GPa).[15]

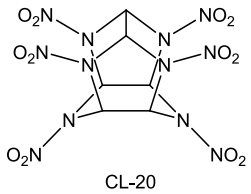


Figure 1. Molecular structure of CL-20.

Given the importance of understanding the behaviour of CL-20 under extreme conditions, the aim of the current study was to determine the structure of the high-pressure ζ-form and obtain information on its phase stability. In order to achieve this, it proved essential to use a combination of x-ray single crystal and powder diffraction techniques. A polycrystalline sample of γ-CL-20 was loaded into a diamond-anvil cell with Fluorinert (FC-77) as the pressure-transmitting medium. The γ-form was observed to persist on compression up to 0.72(5) GPa, but at the next pressure point [1.44(5) GPa] a dramatic change was observed in the powder diffraction pattern, indicative of a phase transition to the high-pressure ζ-form (see Figure 2).

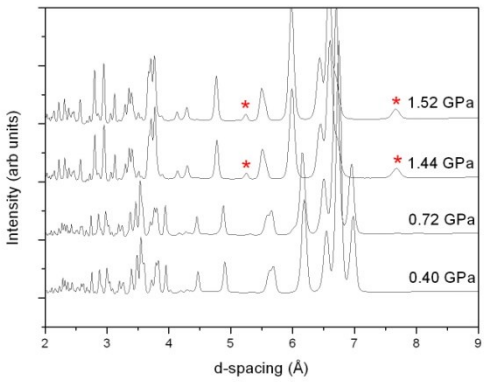


Figure 2. Comparison of the x-ray powder diffraction patterns collected for γ-CL-20 (0.40 and 0.72 GPa) and ζ-CL-20 (1.44 and 1.52 GPa). The red asterisks show the diagnostic peaks of the ζ-form.

Despite the high quality data, attempts to index these patterns gave several possible solutions, none of which allowed structure solution. However, an important observation was that the difference between the x-ray powder diffraction patterns collected for γ- and ζ-CL-20 was subtle. Combined with previous optical observations,[14] this suggested that hydrostatic compression of a single crystal through the γ → ζ transition might retain the integrity of the crystal, *i.e.* the phase transition is not reconstructive. For this reason we turned to single crystal x-ray diffraction and a single crystal of γ-CL-20 was loaded into a diamond-anvil cell with Fluorinert as the pressure-transmitting medium. This crystal was initially compressed to ~0.05 GPa to check crystal quality and the diffraction data were sufficiently good for a full structural refinement of the γ-form. On compression to 1.20(5) GPa, it proved possible to index a set of reflections to a monoclinic cell, space group $P2_1/n$, with a = 12.8244(8), b = 7.9029(8), c = 14.3622(6) Å and β = 111.205(4)°. A second data-set with longer exposure times was recorded at 3.30(5) GPa in an attempt to improve data quality. Due to the limitations of high-pressure data collections caused by shading from the steel body of the diamond-anvil cell, these data-sets suffered from low completeness (*ca.* 60%). This, along with the complexity of the molecular structure, meant that structure solution *via* direct methods was not possible. Instead the indexing solutions obtained from the single crystal studies were used as a starting point for structure solution from the powder diffraction data using the program FOX.[16] This solution was then refined (with no restraints) against each of the single crystal data-sets to give the representative molecular conformation shown in Figure 3.

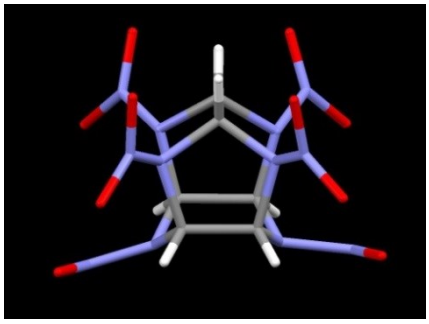


Figure 3. Molecular conformation of ζ-CL-20 obtained at 3.3(5) GPa.

Further corroboration that the crystal structure was correct was obtained by performing full-profile Rietveld refinements on all of the collected powder diffraction patterns, including those kindly supplied by Gump and Peiris.[17] During the refinements, soft constraints were applied to the geometry of the nitro groups, whilst the positions of the cage atoms were constrained to those obtained from the single crystal refinements. Figure 4 shows an example of the quality of the Rietveld refinement for the diffraction pattern collected at 1.44(5) GPa.

In order to facilitate comparison, the molecular structure in the ζ-form is presented alongside that for the γ-form in Fig 5. This comparison shows that the isowurtzitane cage remains unchanged and it is the *exo*- and *endo*- spatial orientation of the nitro groups with respect to the five- and six-membered rings that varies.[9] Figure 5 clearly shows that the high-pressure ζ-form adopts the conformation in which all of the nitro groups are *exo* with respect to the five- and six-membered rings.

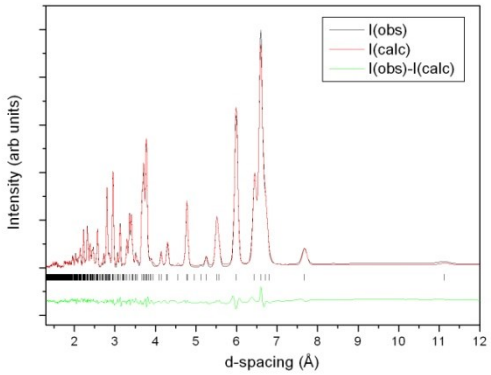


Figure 4. Rietveld refinement of the x-ray powder diffraction pattern recorded at 1.44(5) GPa.

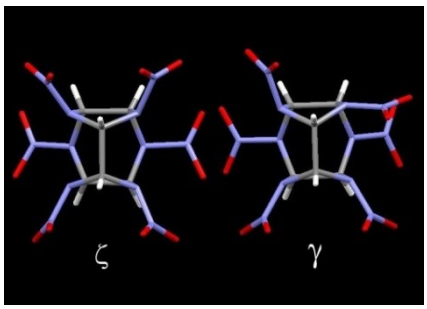
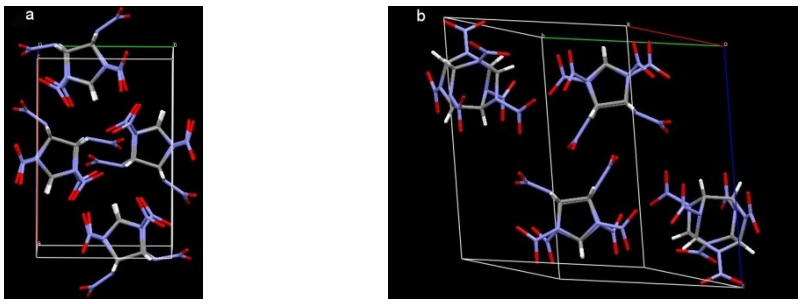


Figure 5. Molecular structure of the ζ-form compared with that of the γ-form.

DFT calculations have explored the relative energies of a range of conformations and have found that there are four conformations that are energetically favourable on steric grounds.[18] The relative energies of these are: ζ-form (9.63 kJ mol^{-1}), ε-form (6.99 kJ mol^{-1}), γ- and α-forms (4.73 kJ mol^{-1}), and β-form (0.0 kJ mol^{-1}). Given these relatively small energy barriers, it is perhaps not surprising that compression of the γ-form will induce a phase transition to a conformation that allows more efficient crystal packing, as is exemplified in this case by the contraction in volume across the γ → ζ transition. The packing in the ζ-form does retain the 'face-to-face' arrangement observed in the γ-form (where all five-membered rings of

the cage are oriented about the same axis, see Figure 6). However, the closer packing and more symmetrical molecular conformation in the ζ-form means that a network of weak C-H…O interactions is observed whereas in the γ-form these interactions form chains. This network arrangement is more like that observed in ε-CL-20, which displays 'edge-to-face' packing. In this way, the ζ-form may be considered to display structural similarities with both γ- and ε-CL-20.



(a) (b)

Figure 6. (a) The 'face-to-face' packing observed in ζ-CL-20; (b) the 'edge-to-face' packing of the ε-form. In both cases the unit cells are oriented such that the five-membered rings are viewed from above.

Based on the unit-cell volumes reported in reference 11, our results show that over the pressure range 1.2-3.5 GPa the ζ-form has a lower density than the ε-form at any given presssure. On this basis, the detonation velocity of the ζ-form would be expected to be lower than that of the ε-form. As has been observed by other authors,[8,10,14] all attempts to recover the ζ-form to ambient pressure were unsuccessful and instead resulted in the formation of the γ-form. This presumably reflects the relatively low barrier to interconversion between the two molecular conformations and so it seems unlikely that recovery could be achieved unless low temperatures were employed.

Conclusions

The crystal structure of the high-pressure ζ-form of CL-20 has been determined using a combination of x-ray single crystal and powder diffraction techniques. Conformational changes in the orientation of the nitro groups of the CL-20 molecule were observed in the γ→ ζ transition, such that molecules in the ζ-form adopt the conformation in which all of the nitro groups are *exo* with respect to the five- and six-membered rings. The ζ-form also displays structural similarities to both the γ- and ε-forms. The level of complexity of this crystal structure extends the limits to which high-pressure techniques may be applied, and higlights the need for employing a range of different methods for structure solution. In addition to solving a long-standing problem

of great significance to the energetics community, the experimental results presented here will be of particular value to computational chemists seeking to model structural changes in energetic materials under extreme conditions, and will allow validation of the intermolecular potentials used to describe this important class of nitramines.

Notes and references

[‡] Crystalline samples of CL-20 were obtained from Dstl. Powder and single crystals of the γ-form were prepared respectively by heating the ε-form to ca. 350 K and by crystallisation from hot benzene. High-pressure x-ray experiments were performed using a Merrill-Bassett diamond-anvil cell[19] equipped with 600 μm culets and a tungsten gasket with a 300 μm hole. Fluorinert FC-77 was used as a hydrostatic pressure medium with a ruby chip acting as pressure calibrant.[20] X-ray diffraction intensities were collected using Mo-Kα radiation on a Bruker SMART APEX II CCD diffractometer.[21] Single crystal data were processed in accordance with the procedure described by Dawson *et al*.[22] X-ray data: ζ-phase $C_6H_6N_{12}O_{12}$ M = 438.19, monoclinic, space group $P2_1/n$, a = 12.579(2), b = 7.7219(19) , c = 14.1260(15) Å, β = 111.218(10)°, V = 1279.1(4) Å^3, T = 293 K, P = 3.30(5) GPa, Z = 4, μ = 0.218 mm^{-1}, D_c = 2.275 Mg m^{-3}, λ = 0.71073 Å, θ_{max} = 23.345°, 5107 reflections measured, 935 unique (R_{int} = 0.128). Final residual for 121 parameters were R_1 = 0.0891, wR_2 = 0.1096 for $I > 2\sigma(I)$, and R_1 = 0.1710, wR_2 = 0.2468 for all data. X-ray powder diffraction data were collected at the Extreme Conditions Beamline, (I15) at the Diamond Light Source, Harwell Science and Innovation Campus, UK. Powder diffraction data were processed using FIT2D[23] and refined using GSAS.[24]

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